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ON HEAT-TREATABLE COPPER-CHROMIUM ALLOY, I.

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ON HEAT-TREATABLE COPPER-CHROMIUM ALLOY (I)*

Shigeyasu Koda and Eiji Isono**

I. Introduction ***/213

Equilibrium diagrams of Cu-Cr alloy have been prepared by Hindrichs (Reference 1) in 1908 and by Siedschlag (Reference 2) in 1923. Both of the reports show the solid solution of Cu but do not show the change in the solid solution by temperature. In 1927, Corson (Reference 3) found the change of solid solution of Cr in Cu-Cr alloy by temperature for the first time, and also found the possibility of changing properties by heat treatment. Thereafter, the study of solid solution of the alloy by temperature change has been announced by Alexander (Reference 4) in 1939 and by Hibbard (Reference 5) in 1948. Since the results of their studies are consistent, they are considered as right. Fig.1 shows the results. /214

As shown in this figure, physical properties of the alloy which contains 0.2 to 0.5% of Cr can be improved by quenching and tempering. Corson (Reference 3) says that 39kg/mm² of tensile strength was obtained by heat treatment for the alloy containing 0.6%Cr.

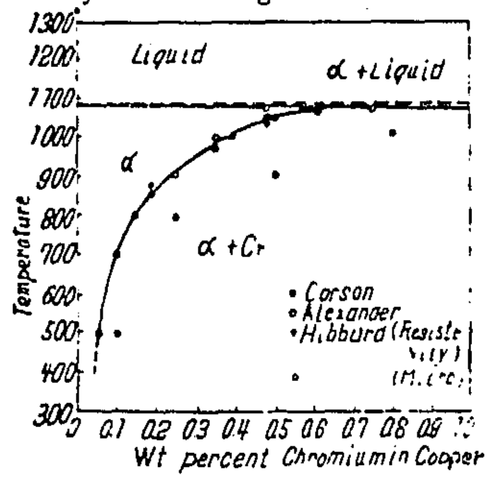

Fig. 1 Equilibrium Diagram of Cu-Cr Alloy.

According to a recent report (Reference 6), in 1947 Goryachov and Smirnov obtained 78kg/mm² of tensile strength and 90% of electrical conductivity for the alloy containing 0.52% Cr by the process of quenching then tempering after working. On the other hand, Alexander (Reference 4) considered Cr significant because he found that the recrystallization temperature of Cu can be increased about 100°C and the abnormal growth of crystal grain at a high temperature

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*** Numbers in margin indicate foreign pagination

	Conductivity	Tensile strength	Elongation
Quenched and tempered at 5000° for 1 hr.	91 %	39 kg/mm²	18 %
Quenched, cold-drawn (75 % reduction) and tempered at 500° for 1 hr.	90 %	42 kg/mm²	9 %
Quenched, cold-drawn (81 % reduction), tempered at 500° for 1 hr. and then cold-drawn (88 % reduction)	86 %	62kg/mm²	2 %

of more than 900°C can be prevented by adding Cr.

As mentioned above, Cu-Cr alloy is significant for electric conductor with high tensile strength and high electrical conductivity, therefore the manufacturing methods, age-hardening properties, performance as electrical wire and effects of adding elements, which have been mentioned only briefly in previous reports, are investigated in this report.

II. Manufacturing of Alloy

According to an old report (Reference 7), alloy containing approximately 3% of Cr should be used when chromic oxide, copper and carbon are dissolved in an electric smelting furnace and aluminum containing a high content of Cr should be used when copper oxide and chromic oxide are deoxidized by the Thermit method. But in this test, Cr metal was used. The purity of the Cr used is 97% and the Cu used was the same as copper for electrical purposes.

Test 1: Powdered chrome of -40 mesh was added to the copper which was covered with charcoal and melted in a platinum electric smelting furnace or a coal smelting furnace. But this test failed because of extensive oxidization of Cr. According to the references, the mother alloy containing 10% of Cr was used, but it is very difficult to obtain the alloy by the regular method. Therefore, the following method was used.

Test 2: Powdered Cr and powdered Cu were mixed together with a ratio of 10% of Cr. Then it was put in a vessel. With test equipment of 10 t, a 20mm diameter x 10mm briquet was made under pressure. Then the mother alloy was made from the briquet by sintering in a vacuum condition. Even though 950°C temperature was applied for 5 to 7 hours, it was found by microscope observation that the temperature was still too low and also the time was too short. But it was decided to use this briquet as the mother alloy since it does not break easily (Further detailed tests are planned.)

Test 3: Since the amount of solution was small, the Cu was covered with fluoride and melted in a platinum electric smelting furnace. Then the previously mentioned mother alloy was alloyed to the Cu after deoxidizing with Cu-P (10%) and 10 minutes later the alloy, temperature at 1200°C, was cast in a metal mold of 12mm diameter. An alloy containing 0.5% of Cr was obtained from the 200g of solution of Cu containing 1% of Cr. (Specimen A1)

Test 4: Since the reduction of Cr is large, a high frequency electric smelting furnace was used to melt rapidly. But this test failed because of a large amount of slag from the stirring action.

Test 5: To make a large amount of specimens, a coal smelting furnace was used and the Cu covered with charcoal was melted in graphite. After deoxidizing with Cu-P, the previously mentioned Cu-Cr mother alloy was alloyed and stirred only once (Reference 9). Then it was cast in a preheated metal mold 20 mm square. Two pieces of the specimen weighing approximately 1 kg each were obtained (Specimen A2 and A3). As the results of content analysis, still only 0.5% of Cr was found out of 1% Cr. Thus, there was a 50% loss of Cr. The specimens that it was decided to use for this test and the manufacturing method will be studied in the future. Production of the casting was good. Table 1 shows the analysis results of each specimen.

Table 1 Samples Prepared.

Mark	Cr Content %
A 1	0.49
A 2	0.49
A 3	0.54

III. Processing of Specimens

An ingot 20 mm square was heated at 920 to 980°C for 2 hours then a 12.8 mm diameter bar was obtained by being drawn 3 times. After being heated at 910°C for 1 hour, then quenched in water, a 200mm diameter bar was obtained by being cold-drawn. The reduction is 97% and the working properties in both hot and cold states were very good.

IV. Age-Hardening Properties

1. Preliminary Test

As mentioned in the introduction, Corson (Reference 3) says that Cu-Cr alloy has age-hardening properties, but does not show definite data. To verify the properties, the A1 alloy (Cr 0.49%) which was cast in 12mm diameter, was used. The specimens were quenched in water after being heated at 950°C for 1 hour then tempered at various temperatures varying from 300 to 700°C for 1 hour. Fig. 2 shows the hardness of the specimens. It shows that the specimen tempered at 500°C has the highest hardness.

2. Effect of Quenching Temperature

The A2 alloy (Cr 0.49%) and the A3 alloy were used. At first, the specimens were heated at 950°C, 1000°C and 1040°C for the A2 alloy and 950°C and 1040°C for the A3 alloy for 1 hour then quenched in water. After being tempered at 200 to 700°C for 1 hour, the hardness was investigated. The results were shown in Fig. 3 and 4. It was found that 950°C of quenching temperature /215
is not enough and more than 1000°C of temperature is required. The highest hardness of both of the alloys occurs at 475°C to 500°C of tempering temperature.

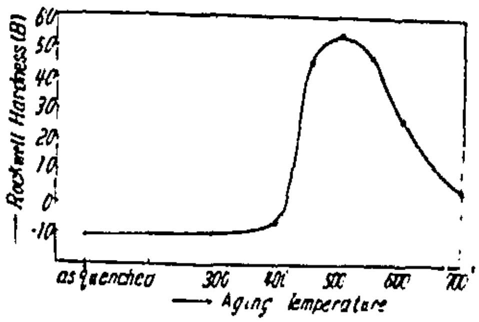

Fig 2 Hardness Change "A 1" Alloy Quenched from 950 and Tempered at Various Temperatures for 1 hr.

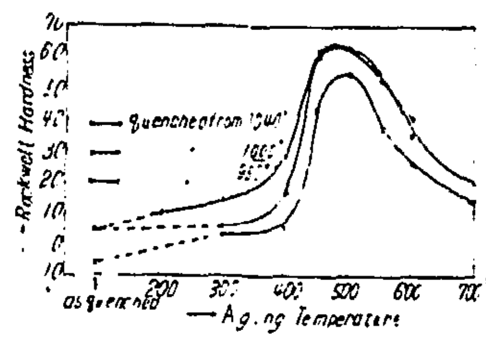

Fig 3 Effect of Quenching Temperature Hardness Change of "A 2" Alloy Quenched from 1040°, 1000° or 950° and Tempered at Various Teperatures for 1 hr.

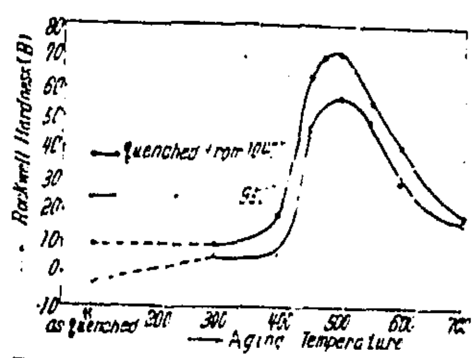

Fig 4 Effect of Quenching Temperature Hardness Change of "A 3" Alloy Quenched from 1040° or 950° and Tempered at Various Temperatures for 1 hr

3. Effect of Tempering Time

Since there were not enough specimens sized 12mm diameter of the A1 alloy, specimens of 7.3mm diameter of A2 and A3 alloy were saved from the previous process. These specimens were tempered at 500°C, 450°C and 400°C with various tempering times after quenching. The variation of the tempering time is from 1 minute to 10 hours. The quenching temperature was 990°C for 1 hour, except the specimen of A3 alloy tempered at 550°C and quenched, after being heated, at 1040°C for 1 hour. Fig. 5 and 6 show the results. For the specimens tempered at 500°C, the specimen tempered 1 hour has the highest degree of hardness. For the specimens tempered at 450°C, the specimen tempered 3 hours has the highest degree of hardness.

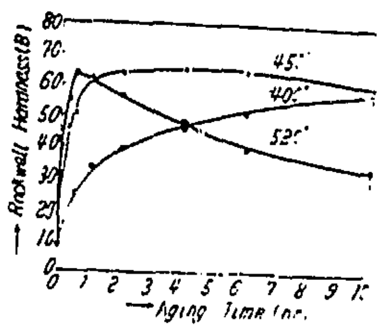

Fig. 5 Effect of Tempering Time. The Result of "A 2" Alloy.

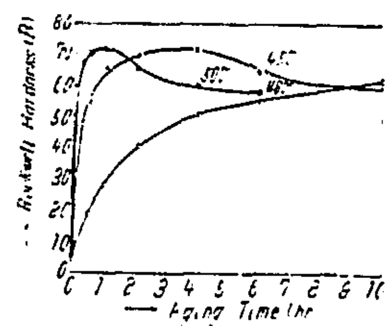

Fig. 6 Effect of Tempering Time. The Result of "A 3" Alloy.

V. Softening Temperature by Annealing

As mentioned in the Introduction, Alexander (Reference 4) says the softening temperature can be increased by annealing for worked material of Cu-Cr alloy. This is investigated by testing hardness. The specimens were taken from the A3 alloy which was in the process of being drawn to 8.2mm diameter after quenching at 12.8mm diameter. Then the specimens were tempered at 520°C for 1 hour. After tempering, the specimens were drawn to 5.6mm diameter. The specimens were annealed at various temperatures, 100°C through 700°C for 1 hour (reduction 53%). As shown in Fig. 7, softening of the specimens did not occur at the temperatures of up to 500°C for 1 hour of annealing.

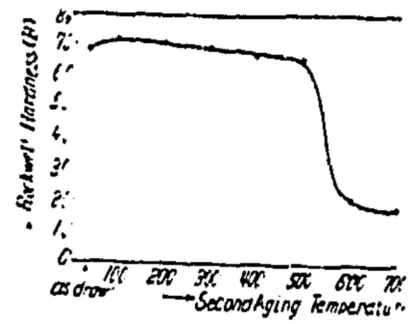

Fig. 7 Effect Annealing The Samples are Cold-worked "A 3" Alloy (The reduction percentage is 53 %).

VI. Properties for Electrical Wire

To obtain excellent properties for electrical wire, the following 3 methods were taken by combining cold-working and heat treatment relevant to the previous test results. /216

1. Q-T method: After finishing final diameter, quenched and tempered.
2. Q-W-T method: Cold-drawn after heat treatment then tempered.
3. Q-W-T-W-T method: After quenching cold-drawn to intermediate diameter, tempered then cold-drawn again and then tempered.

1. Q-T Method

The A2 alloy was cold-drawn to 2mm diameter then, after solution treatment at 1000°C for 1 hour, quenched in water. It was tempered at various temperatures, 100 to 600°C, for 1 hour after quenching, the regular ways of quenching and tempering were used. The properties are shown in Fig. 8. The curves are similar to the previous hardness change curves. The quenching temperature at the maximum electrical conductivity is 50°C higher than that of the maximum tensile strength.

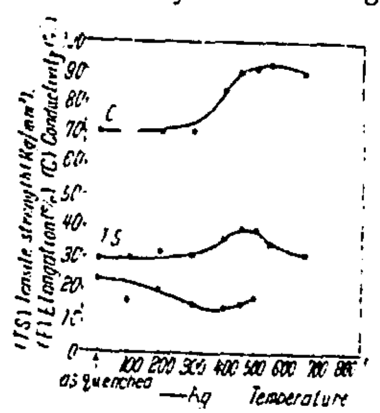

Fig 8 Properties of "A 2" Alloy Wires which were Quenched and Tempered at Various Temperatures for 1 hr (Q-T treatment).

2. Q-W-T Method

This method has the cold-drawn process between quenching and tempering. The first method is solution treatment at 910°C for 1 hour for 12.8mm diameter specimens then quenched in water. After quenching, they were cold-drawn to 2mm diameter and then tempered at various temperatures, 100 to 800°C, for 1 hour. As shown in Fig.9, the curve of tensile strength has a peculiar bump showing from hardening from tempering during softening. There is considerable difference in the aging temperature between the peak of the bump and the maximum electrical conductivity.

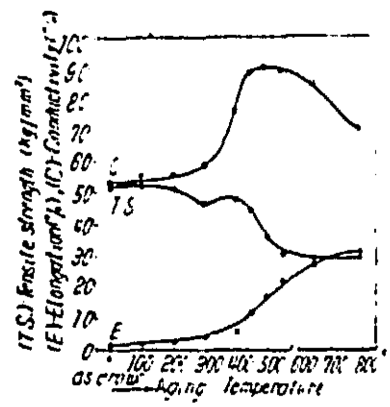

Fig 9 Properties of "A 2" Alloy Wires which were Quenched, Cold-drawn (reduction. 75%) and Tempered for 1 hr (Q-W-T) treatment.

The second method is that the specimens were given the solution treatment at 981°C for 1 hour after being cold-drawn to 4.2mm diameter, then quenched in water. After quenching they were cold-drawn again to 2.0mm diameter and then tempered at various temperatures, 100 to 800°C for 1 hour. While the reduction of the first method is 97.6%, that of the second method is 75%. As shown in Fig. 10, a peculiar increasing curve in tensile strength can be seen. It is interesting that the aging temperature of the maximum tensile strength is close to that of the maximum electrical conductivity. Compared with the Q-T method, the tensile strength is 10kg/mm^2 higher for about the same electrical conductivity. The elongation at that temperature is as high as 9%.

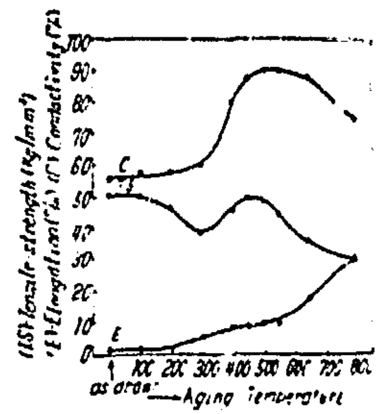

Fig. 10 Properties of "A 2" Alloy Wires which were Quenched. Cold-drawn (reduction 97.6 %) and Tempered for 1 hr (Q-W-T2 Treatment).

3. Q-W-T-W-T Method

This method has tempering in the process. In the first process, specimens of 12.8mm diameter were quenched in water after solution treatment at 910°C for 1 hour. Then, when they were cold-drawn to 8.2mm diameter (Reduction:59%), they were tempered at 550°C for 1 hour and then cold-drawn to 2.0mm diameter, the final diameter. After this cold work, they were tempered again at various temperatures, 100 to 800°C for 1 hour. Fig. 11 shows their properties. High tensile strength and electrical conductivity were obtained on the wire specimens which did not have the last tempering even though the elongation is small. Probably because of a too high tempering temperature at the intermediate process, there is no tendency to better properties such as the specimens tempered by the Q-W-T method show. /217

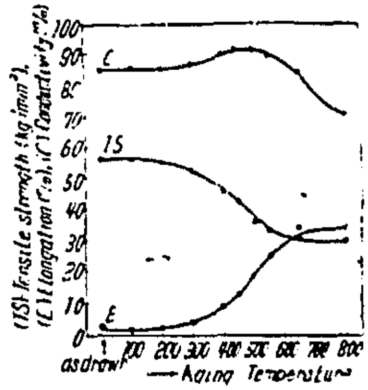

Fig 11 Properties of "A 2" Alloy Wires which were Quenched. Cold-drawn to Intermediate Diameter (reduction, 59 %) Tempered, at 550° for 1 hr Cold-drawn Again (reduction, 94 %) and Tempered (Q-W-T-W-T treatment).

In the second process, the specimens were tempered at 550°C for 1 hour at 5.6mm diameter in the intermediate process. The third process is the same as the second process except that the tempering temperature was 500°C for 1 hour. Fig. 12 and 13 show the test results from the second process and the third process. In both cases, precipitation hardening was not obtained after the last tempering because of concentrating too much on better electrical conductivity at the intermediate tempering stage.

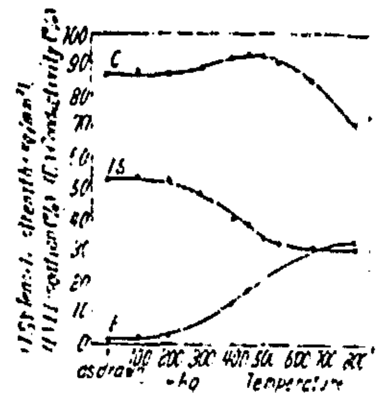

Fig 12 Properties of "A 2" Alloy Wires which were Quenched, Cold-drawn to Intermediate Diameter (reduction 81 %), Tempered at 550 for 1 hr, Cold-drawn Again (reduction 87.5 %) and Tempered (Q-W-T-W-T2 treatment).

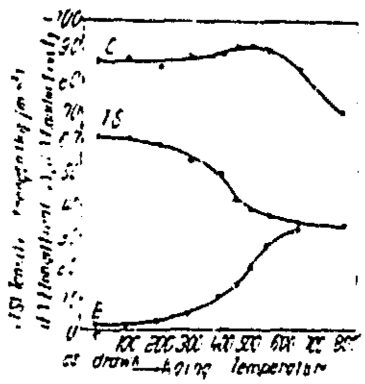

Fig 13 Properties of "A 2" Alloy Wires which were Quenched, Cold-drawn to Intermediate Diameter (Reduction, 81 %), Tempered at 500 for 1 hr, Cold-dawn Again (reduction, 87.5 %) and Tempered. (Q-W-T-W-T3 treatment).

When considering the test results of the Q-W-T method, better alloy could be obtained if more attention is paid to precipitation hardening.

As a summary of the various tests results, Fig. 14 shows the properties of the specimens prepared by the various processes.

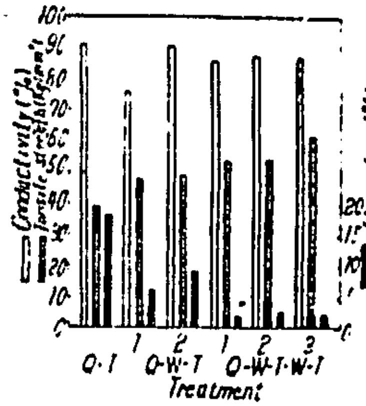

Fig 14 Comparison of Properties of "A" Alloy Wire Which Made by Various Processes.

VII. Considerations

From the test results, the subjected alloy has much better electrical conductivity than Corson alloys (Cu-Ni_2Si group) or copper-cadmium alloys which are very good electrical conductors though its tensile strength is inferior to them. When considering the test results of the second process of the Q-W-T method, the tensile strength could be improved by studying the process before the intermediate and final tempering and the tempering process of the Q-W-T-W-T method. (In the intermediate tempering process of this test, the specimens were over-aged.) Further study and tests for this will be performed.

VIII. Conclusions

Cu-Cr alloy containing 0.5% Cr was made from the mother alloy of Cu-Cr alloy containing 10% Cr by a sintering method and its age-hardening properties and typical properties for electrical wire were studied.

In the test results, it is found that the proper quenching temperature is approximately 1000°C and the proper tempering temperature is 500°C for 1 hour or 450°C for 3 hours. The following properties for electrical wire were obtained from the process of cold-work after quenching then tempering and the process of cold work-tempering-cold work-tempering: electrical conductivity 90%, tensile strength 49 kg/mm^2, elongation 9% or electrical conductivity 86%, tensile strength 62kg/mm², elongation 2%. The working properties in cold and hot were extremely good.

The merit of this alloy as a material for an electrical conductor is good electrical conductivity. Although its tensile strength is inferior to Corson alloys and copper-cadmium alloys, there is a possibility to improve it by studying the processes.

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16. Abstract

A mother alloy of 10% Cr and 90% Cu was prepared by sintering. This was alloyed with the Cu melt and Cu-Cr alloys containing about 0.5% Cr was obtained. These alloys could be deformed easily in both the hot and cold states. By measuring the hardness change age-hardening properties of cast alloys were studied, which had been quenched from 950° and aged at 300°-700° for 1 hour. The maximum hardness was obtained with the tempering temperature of 500°. For the temperature of soln.-treatment, 950° was insufficient and that above 1000° necessary. For the tempering time, a treatment at 500° for 1 hr. or at 450° for 3 hrs. yielded the maximun hardness. As for the properties for electrical conductors, 3 kinds of wires (diam. 2 mm.) were made: (1) after cold-drawn to 2 mm., soln.-treated, quenched, and then tempered (500°, 1 hr.); (2) after quenching, cold-drawn (75% reduction) to 2 mm. and tempered (500°, 1 hr.); (3) after quenching, cold-drawn (81%) to intermediate diameter, tempered (500°, 1 hr.) and then cold-drawn (88%) again Properties obtained for the 3 kinds, respectively, were as follows: Cond. 91, 90, and 86%. Tensile strength and strength for electrical cond. are given.

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